JUNE 12TH, 1929

QUANTUM ANALYSIS OF THE BERYLLIUM OXIDE BANDS

PERTURBATIONS IN BAND SPECTRA

STANFORD UNIVERSITY
FEB
4
1930

This thesis has been accepted by the GRADUATE SCHOOL OF NEW YORK UNIVERSITY in partial fulfillment of the requirements for the degree of Doctor of Philosophy

STANFORD UNIVERSITY LIBRARIES
WITHDRAWN

JENNY EUGÉNIE ROSENTHAL

3781
N53R
UNCLASSED
L. C.
DISSERTATION

QUANTUM ANALYSIS OF THE BERYLLIUM OXIDE BANDS

BY

JENNY E. ROSENTHAL AND F. A. JENKINS

Reprinted from PHYSICAL REVIEW, pp. 163-168, Vol. 33, No. 2, February, 1929

QUANTUM ANALYSIS OF THE BERYLLIUM OXIDE BANDS

By Jenny E. Rosenthal and F. A. Jenkins

Abstract

New measurements of the structure lines in the (0, 0), (1, 1), (0, 1), (1, 2), (1, 0) and (2, 1) bands of the visible BeO system are reported. Each band has P and R branches of almost equal intensity, the lines of which are strictly single. There is probably but one missing line at the origin. This structure characterizes the system as $^1S \rightarrow {}^1S$, the odd multiplicity agreeing with the even number of electrons in neutral BeO. The rotational terms are investigated by the combination principle, and can be represented by $F(j) = Bj(j+1) + D[j(j+1)]^2 + \cdots$ with j integral as required for ^1S states. One perturbation is found, consisting of a displacement of the line $R(49)$ in the (1, 0) band by 0.45 cm^{-1} toward lower frequencies, with no sign of doubling. The following equation is obtained for the null-lines: $\nu_0 = 21{,}254.05 + 1370.81(n' + \frac{1}{2}) - 7.76(n' + \frac{1}{2})^2 - 1487.45(n'' + \frac{1}{2}) + 11.87(n'' + \frac{1}{2})^2$.

Molecular constants of BeO.—The principal molecular constants, evaluated from rotational term-differences using the new quantum mechanics energy formula, are: $B_0' = 1.5771$, $B_0'' = 1.6514$, $\alpha' = -0.0160$, $\alpha'' = -0.0186$, $D_0' = -8.44 \times 10^{-6}$, $D_0'' = -8.26 \times 10^{-6}$, $\beta' = +0.03 \times 10^{-6}$, $\beta'' = -0.06 \times 10^{-6}$, $F_0' = 22 \times 10^{-12}$, $F_0'' = 12 \times 10^{-12}$, the zero subscripts referring to the vibrationless condition. The nuclear separation in the final state is: $r_0'' = 1.327 \times 10^{-8}$ cm.

THE spectrum obtained by introducing beryllium or beryllium salts into the arc in air shows a system of bands in the visible region consisting of several sequences which degrade toward the red. The stronger band heads were first measured by Hartley, and later by Lecoq de Boisbaudran and by de Gramont.[1] The spectrum was investigated in more detail by L. C. Glaser, [2,3] using the second order of a 10-foot grating. In addition to more accurate and complete measurements of the heads, Glaser gave a table of the structure lines of the strongest sequence, that in the blue with its first head at λ4708. The lines of the first band he arranged in four series α, β, γ, δ. As will be shown below, this division cannot be justified, a fact which is not surprising since the work was done before the development of the present theory of band spectra. His attempts to find numerical relations between these bands and the AlO bands of the aluminum arc[4] were doubtless due to the marked similarity of the two spectra in many respects.

According to the view we wish to support, these beryllium bands are also due to the oxide, BeO. Some of Glaser's experiments give evidence for this; in particular he found that with the arc between metallic Be electrodes, the bands are much weaker in vacuum than in air. Further experimental evi-

[1] For a summary and comparison of the earlier results see Kayser and Konen, "Handbuch der Spectroscopie" **VII**, 102 (1924).

[2] L. C. Glaser, Dissertation, Berlin (1916).

[3] Glaser, Ann. d. Physik **68**, 73 (1922).

[4] W. C. Pomeroy, Phys. Rev. **29**, 59 (1927).

dence has recently been obtained by Jevons,[5] who finds this group of bands to be relatively stronger in the outer part of the flame surrounding the arc in air. Combining these observations with the theoretical confirmation to be given below, there seems to be little doubt as to the identity of the emitter. The purpose of the present communication[6] is to give the quantum interpretation of the rotational structure of the bands of this system. It is based on new measurements of the lines of the six strongest bands made from plates on which the dispersion and resolution are roughly double those reached by Glaser.

The spectrograms. A horizontal carbon arc with both poles cored with a mixture of equal parts of powdered potassium beryllium fluoride and carbon dust proved to be a very satisfactory source. With an average current of about 5 amp, a pale blue flame tinged with yellow appeared above the poles. An image of this flame was thrown on the slit of the 21 foot concave grating

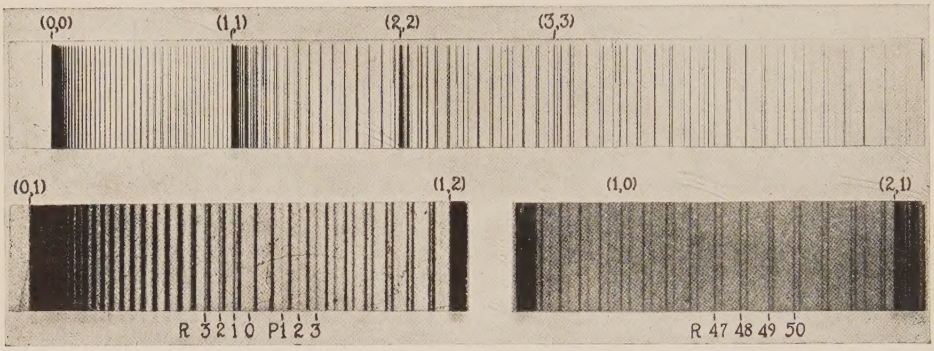

Fig. 1. *a.* Strongest sequence of BeO bands. Iron arc comparison spectrum. *b.* First part of (0, 1) band, showing intensity anomalies near the origin. The line $R(1)$ is exceptionally strong, while $R(0)$ is weaker than the corresponding line, $P(1)$. *c.* Region λλ 4435–4450 of the (1, 0) band. The perturbation of $R(49)$ shows as a discontinuity in the width of the doublets formed by R and P lines.

spectrograph.[7] The spectrum thus obtained consisted of the ultra-violet BeF bands,[8] the BeO bands in the blue and green, and the stronger bands of the green CaF sequence,[9] as well as atomic lines of Be, Ca, Fe, Mn and other impurities. Comparison lines of the iron arc were used[10] and their exact coincidence with the Fe lines appearing in the band exposure eliminated the possibility of accidental shifts.

[5] W. Jevons, Proc. Roy. Soc. (in press). We are indebted to Professor Jevons for making this article available to us in manuscript, as well as a copy of Glaser's work referred to above.[2]

[6] A preliminary account of this investigation was given in a paper before the American Physical Society at the New York meeting, February, 1928, Phys. Rev. **31**, 705 (1928).

[7] The plates were taken by one of the writers (F. A. J.) while a National Research Fellow at Harvard University. The characteristics of the grating and its mounting are described in Phys. Rev. **30**, 438 (1927).

[8] S. Datta, Proc. Roy. Soc. **A101**, 187 (1922).

[9] Datta, Proc. Roy. Soc. **A99**, 436 (1921).

[10] Wave-lengths as given by Meggers, Kiess and Burns, Bull. Bur. Stan. **19**, 263 (1924).

The strong group in the blue (Fig. 1*a*), according to the vibrational quantum number assignment made by Mecke,[11] is the sequence having $n''-n'=0$. The two adjacent sequences, $+1$ and -1, were also suitable for measurement. The $+2$ sequence found by Glaser and the few bands of the

TABLE I. *Lines in the visible BeO bands.* The columns of ν_{vac} for the lines of each band are headed by its vibrational quantum numbers and λ_{air} of the band head.

	(0,0) band λ4708.636		(0,1) band λ5054.415		(1,1) band λ4732.618		(2,1) band λ4451.664	
J	$R(J)$	$P(J)$	$R(J)$	$P(J)$	J	$R(J)$	$P(J)$	$R(J)$	$P(J)$
0	21,199.81				1				
1	202.88	21,193.25	19,739.14	19,729.70	2	21,097.30			
2	205.74	189.97	742.07	726.39	3	099.76		22,439.22	
3	208.52	186.41	744.89	722.96	4	102.41	21,074.47	—	
4	211.12	182.66	747.58	719.36	5	104.82	070.69	444.00	22,410.20
5	213.58	178.88	750.21	715.73	6	107.12	066.71	446.14	—
6	215.58	174.82	752.63	711.95	7	109.19	062.61	447.93	401.84
7	217.71	170.65	754.96	708.02	8	111.20	058.37	449.68	397.49
8	219.65	166.35	757.19	704.04	9	112.99	054.02	451.23	392.84
9	221.43	161.93	759.40	699.92	10	114.68	049.50	—	388.11
10	223.12	157.28	761.48	695.70	11	116.32	044.91	—	383.11
11	224.62	152.57	763.43	691.45	12	—	040.13	454.75	378.03
12	225.92	147.70	765.30	686.89	13	118.65	—	455.47	372.76
13	227.23	142.69	767.03	682.33	14	120.05	030.17	456.18	367.29
14	228.40	137.53	768.64	677.82	15			456.70	361.70
15	229.34	132.22	770.12	673.05	16			457.23	355.95
16	230.08	126.75	771.51	668.22	17				350.00
17	230.67	121.01	772.79	663.26	18				343.89
18	230.94	115.39	773.95	658.20					
19	—	109.40	774.98	653.06		(1,0) band λ4427.312		(1,2) band λ5075.726	
20	231.61	103.48	775.90	647.79	J	$R(J)$	$P(J)$	$R(J)$	$P(J)$
21	231.61	097.30	776.68	642.40					
22	—	090.96	777.37	636.95	0	22,555.06		19,651.13	
23	230.94	084.52	777.92	631.35	1	558.23		654.04	
24	230.67	077.93	778.40	625.65	2	560.82		657.07	19,641.47
25	230.08	071.17	778.84	619.92	3	563.51		659.76	638.05
26	229.34	064.31	779.18	614.00	4	565.93		662.56	634.56
27	228.40	057.30	779.18	608.04	5	568.11	22,534.03	665.09	630.93
28	227.53	050.17	779.18	601.94	6	570.16	529.79	—	627.28
29	226.33	042.88	779.18	595.66	7	571.98	525.41	669.89	623.43
30	224.94	035.41	778.84	589.35	8	573.67	520.90	672.26	619.48
31	223.48	027.85	778.40	582.92	9	575.17	516.23	674.46	615.49
32	221.75	020.03	777.92	576.38	10	576.49	511.34	676.57	—
33	219.95	012.30	777.37	569.76	11	577.65	506.27	678.55	607.29
34	218.01	004.20	776.68	563.04	12	578.57	501.08	680.49	602.81
35	215.97	996.02	775.90	556.20	13	579.29	495.63	682.32	598.54
36	213.58	987.65	774.98	549.24	14	579.87	490.09	683.93	594.06
37	211.12	979.40	773.95	542.27	15	580.30	484.34	685.52	589.36
38	208.52	970.73	772.79	535.08	16	—	478.39	686.98	584.61
39	205.74	962.02	771.51	527.90	17	580.79	472.16	688.32	579.73
40	202.88	953.18	770.12	520.51	18	—	466.09	689.60	575.01
41	199.81	944.17	768.64	513.02	19	580.30	459.64	690.70	569.84
42	196.56	935.02	767.03	505.50	20	579.87	452.83	691.71	564.85
43	193.25	925.77	765.30	497.86	21	579.12	446.14	692.64	559.73
44	189.67	916.36	763.43	490.05	22	578.28	439.22		
45	185.94	906.74	761.48	482.23	23	577.25	432.17		
46	182.11	897.07	759.40	474.37	24	576.06	424.86		
47	178.16	887.12	757.19	466.16	25	574.68	417.33		
48	173.97	877.08	754.80	458.01	26	573.10	409.68		
49	169.61	867.05	752.33	449.75	27	571.35	401.84		
50	165.15	856.75	749.71	441.39	28	569.43	393.84		
51	160.53	846.37	747.00	432.89	29	567.30	385.64		
52	155.72	835.82	744.19	424.31	30	564.94	377.32		
53	150.73	825.20	741.25	415.66	31	562.47	368.76		
54	145.57	814.25	738.17	406.89	32	559.76	360.13		
55	140.29	803.32	735.00	398.01	33	556.95	351.19		
56	134.87	792.21	731.67	389.03					
57	129.25	780.97	728.23	379.92					
58	123.58	769.48	724.65	370.72					
59	117.51	758.09	721.00	361.49					
60		746.40							
61		734.59							

-2 sequence recently added by Jevons[5] are very faint. Accordingly, measurements have been made of the lines of the first two bands in each of the three stronger sequences, using the second order except for the (0, 1) and (1, 2)

[11] R. Mecke, Phys. Zeits. **26**, 217 (1925).

bands, which were measured in the first order. The mean error for each line should not in general exceed 0.03 cm^{-1}. In some instances, however, because of superposition by atomic lines (particularly in the -1 sequence) and by other strong band lines, larger errors were unavoidable. Table I contains the wave-numbers in vacuum of all lines measured. In view of these numerous cases of superposition and overlapping of series, the intensity data are of very little value and have therefore been omitted.

Structural features of the bands. Since the bands of each sequence are closely grouped, the system is of the familiar type in which the vibration frequency and moment of inertia are only slightly changed by the electron transition. The vibrational intensity distribution is also characteristic of this type, resembling that of the violet CN bands in the arc. Hence there could be no doubt as to the correct assignment of vibrational quantum numbers. A complete description of the vibrational structure is given by Jevons[5] who finds that the heads are closely represented by:

$$\nu_h = 21,287.0 + 1364.2(n'+\tfrac{1}{2}) - 5.90(n'+\tfrac{1}{2})^2 - 1479.1(n''+\tfrac{1}{2}) + 15.22(n''+\tfrac{1}{2})^2 - 5.24(n'+\tfrac{1}{2})(n''+\tfrac{1}{2}) \quad (1)$$

The rotational structure is of the simplest possible type, each band having one R and one P branch of strictly single lines. Resolution is complete except for 4 or 5 lines at the head, and in the (0, 0) band about 70 members of each branch can be traced reaching a maximum of intensity between $j = 30$ and 35 and extending over several other bands of the sequence. There is no sign of splitting into finer components even for the last lines. The α and β series of Glaser together make up the P branch, alternate lines belonging to one or the other. His γ and δ series form the R branch in a similar way.

Difficulty was encountered in establishing the number of missing lines, although the bands are well resolved in the neighborhood of the origin, which is far from the head. In the (0, 0) band, coincidence with the R lines returning from the head prevents any decision. The region of the origin in the (1, 0) band is obscured by a diffuse atomic line. The best evidence was obtained from the (0, 1) band. Here it appears that but one line is missing, although the first P line is extremely weak, and the first R line even stronger than two subsequent lines of this branch (Fig. 1*b*). The latter anomaly is very probably due to coincidence with the Ti line λ5064.66. No evidence was found of a Q branch, although a systematic search was made for Q lines of low intensity.

In the (1, 0) band a perturbation occurs which is obvious even on casual inspection (Fig. 1*c*). The line $R(49)$ is displaced 0.45 cm^{-1} toward lower frequencies from its expected position. The fact that no splitting or intensity change occurs is further evidence for the true singlet character of the lines. The corresponding line in the (0, 0) band is not perturbed, so the irregularity must be in the initial state $n' = 1$, $j' = 50$.

Rotational term analysis. Calling the first lines of the two branches $R(0)$ and $P(1)$ it was found at once that the combination relations between the R

and P branches[12] agreed among the bands in the manner to be expected. The extent of this agreement is shown graphically in Fig. 2. The combination differences $\Delta_2 F$ for low quantum numbers are represented closely by $4B(j+\frac{1}{2})$ where $j=0, 1, 2 \cdots$. Since there is probably only one line missing near the origin and since the bands show no evidence of electronic multiplicity, the assumption is justified[13] that there is no resultant electronic angular momentum in either initial or final states. Hence the system arises from a transition

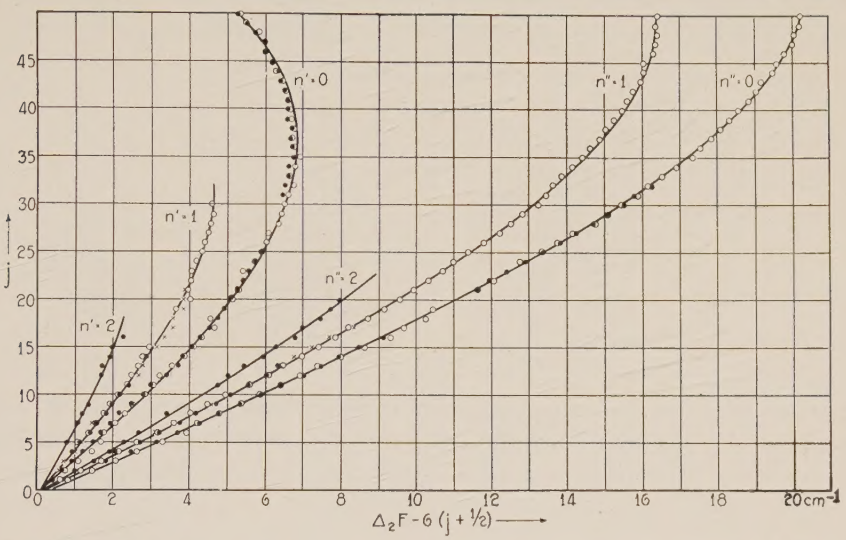

Fig. 2. Combination differences. The solid lines represent the values calculated by Eqs. (2) and (3). The linear function $6(j+\frac{1}{2})$ has been subtracted from $\Delta_2 F$ to magnify the scale. For the initial states circles, dots and crosses represent data from bands having $n''=0$, 1 and 2, respectively. Similarly, for the final states they refer to bands with $n'=0$, 1 and 2.

between two $^1S_0$ molecular terms and is strictly analogous to the CuH bands. In a ^1S state the accurate expression for the rotational term-difference is, using the j values of the new quantum mechanics,

$$\Delta_2 F(j)=4B_n(j+\tfrac{1}{2})+8D_n(j+\tfrac{1}{2})^3+12F_n(j+\tfrac{1}{2})^5+\cdots \qquad (2)$$

Following the method suggested by Birge[14] the constants B_n were evaluated by least squares, using the theoretical relations for D_n and F_n.[15] The results of this calculation are

$$\begin{aligned} B_n' &= 1.5771-0.016(n'+\tfrac{1}{2}), & B_n'' &= 1.6514-0.0186(n''+\tfrac{1}{2}), \\ D_n' &= \{-8.44+0.03(n'+\tfrac{1}{2})\}10^{-6} & D_n'' &= \{-8.26-0.06(n''+\tfrac{1}{2})\}10^{-6} \\ F_n' &= 22\times 10^{-12} & F_n'' &= 12\times 10^{-12}. \end{aligned} \qquad (3)$$

[12] R. T. Birge, Bull. Nat. Res. Council No. 57, p. 145 (1926).

[13] R. S. Mulliken, Phys. Rev. **28**, 481 (1926).

[14] Ref 12, p. 174.

[15] Account was taken of the variation of D_n with n (ref. 4, Eq. (19)). F_n was taken as the same for $n=0$, 1 and 2.

From the constant terms in the equations for B_n, the following values of the moment of inertia I_0 for the vibrationless molecule and of the corresponding internuclear distances r_0 are obtained:

$$I_0' = 17.564 \times 10^{-40} \text{ gr cm}^2 \qquad I_0'' = 16.774 \times 10^{-40}$$

$$r_0' = 1.358 \times 10^{-8} \text{ cm} \qquad r_0'' = 1.327 \times 10^{-8}$$

B_n was evaluated separately for each band, and the agreements shown in Table II furnish conclusive evidence that the assignment of vibrational numbers is correct. This table also includes the band-origins, ν_0, each of which is

TABLE II. *Band constants*

	$n''=$ 0	1	2
n'	$B'=$ 1.5692	1.5689	
0	$B''=$ 1.6421	1.6232	
	$\nu_0=$21,196.76	19,732.99	
1	1.5534	1.5537	1.5537
	1.6422	1.6233	1.6052
	22,552.15	21,088.28	19,648.00
2		1.5363	
		1.6231	
		22,428.20	

the mean of a set of values obtained from several lines of both R and P branches. By the term formula used, ν_0 is the same as the wave-number of the null-line. The origins are quite accurately given by the equation:

$$\nu_0 = 21,254.05 + 1370.81(n'+\tfrac{1}{2}) - 7.76(n'+\tfrac{1}{2})^2 - 1487.45(n''+\tfrac{1}{2}) + 11.87(n''+\tfrac{1}{2})^2 \qquad (4)$$

Conclusions. The constants of the vibrational energy from Eq. (4) differ markedly from those given by Jevons (Eq. (1)). This is to be expected, since his equation refers to heads, which in the present case are at a rather large, and therefore variable, distance from the origins.

As was mentioned above, the rotational structure conforms in every respect with that to be expected for a band system resulting from a $^1S \rightarrow {}^1S$ electron transition. The odd multiplicity requires[13] that the emitting molecule have an even number of electrons. This definitely excludes BeN and BeH, leaving as possibilities Be_2 or BeO, since ionized molecules do not come into consideration. The experimental evidence favors BeO, as do considerations of stability. The internuclear distance in the final state, the lowest known level of BeO, as compared with the corresponding r_0 values for the oxides of the other elements in the first row of the periodic table seems entirely consistent with this view:

	BeO	BO	CO	NO	O_2
r_0''	1.33	1.21	1.15	1.15	1.20

All of these refer to the normal electronic state, and they evidently show the same general trend as the atomic volume curve for these elements.

NEW YORK UNIVERSITY,
UNIVERSITY HEIGHTS, N. Y.,
November, 1928.

PERTURBATIONS IN BAND SPECTRA. I.

BY

JENNY E. ROSENTHAL AND F. A. JENKINS

Department of Physics, New York University

Reprinted from the Proceedings of the NATIONAL ACADEMY OF SCIENCES,
Vol. 15, No. 5, pp. 381–387, May, 1929.

Reprinted from the Proceedings of the National Academy of Sciences,
Vol. 15, No. 5, pp. 381–387. May, 1929.

PERTURBATIONS IN BAND SPECTRA. I.

By Jenny E. Rosenthal and F. A. Jenkins

Department of Physics, New York University

Communicated March 25, 1929

The series of lines which make up a band in the spectrum of a diatomic molecule show, in certain cases, irregularities which are known as perturbations.[1] When these occur, some of the energy terms involved must deviate from a regular term-formula of the ordinary type. Until recently no theoretical interpretation of these phenomena had been attempted, and the empirical data were few and scattered. However, accurate descriptions are now available of the quantitative relations in perturbations in several spectra. In an article describing some new bands of the violet CN system[2] one of the writers drew attention to two very remarkable perturbations, one in the initial state, b^2S, with vibrational quantum number, $n = 12$, and the other in the final state, a^2S, with $n = 11$. These bands are well resolved and of simple structure, so that accurate values may be obtained for the displacements of the lines from their expected positions in both these perturbations.

The obvious method of studying such cases is to derive a formula to fit the frequencies of the regular lines of the series, and then to plot the deviations of all observed lines from this formula. Such a curve has been given[2] for part of the perturbation in a^2S. It has a form similar to a curve of anomalous dispersion in the region of the resonance frequency. Extending this work, we have now completed the investigation of the deviations in the P branches of the (11,11) and (12,12) violet CN bands. The results are shown in figure 1. Curve a (solid lines) includes all P lines of the (11,11) band, the ordinates representing displacements from the formula

$$\nu = 24{,}499.74 - 3.3262j_1 - 0.03144j_1^2 - 3.00 \times 10^{-5} j_1^3 - 0.822 \times 10^{-6} j_1^4.$$

It shows three points of maximum perturbation, at $j_1 = 13^1/_2$, $25^1/_2$ and $28^1/_2$. The quantum numbers j_1 refer to states in which the spin annular momentum is parallel to that of the nuclei ($j_1 = m + \epsilon$). The R branch shows an exactly similar set of perturbations, and by means of the com-

bination principle the assignment of quantum numbers given in curve *a* could be made certain up to $j_1 = 24^1/_2$. Curve *c* refers to the *P* branch of the (12,12) band, where conditions are more complicated, due to the presence of a doubling in the rotational terms of both initial and final

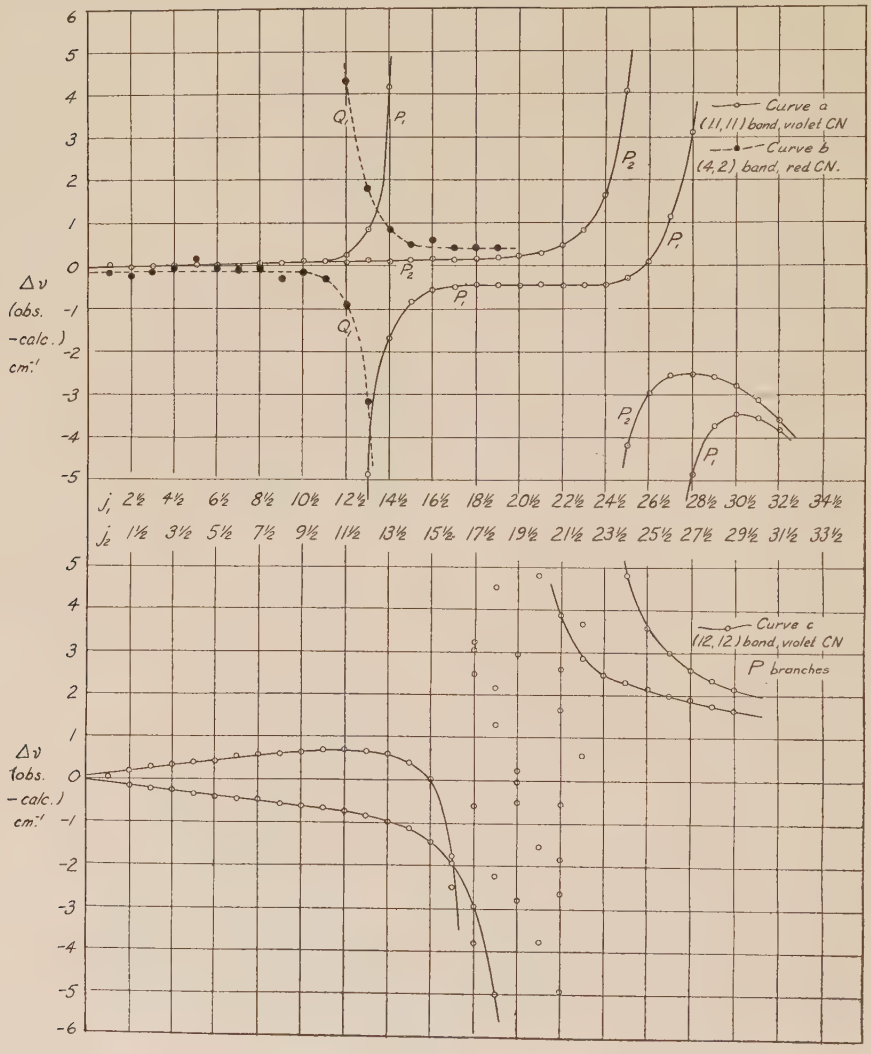
Curve a
(11,11) band, violet CN
Curve b
(4,2) band, red CN.
Curve c
(12,12) band, violet CN
P branches
Δν (obs. - calc.) cm.⁻¹
j₁ 2½ 4½ 6½ 8½ 10½ 12½ 14½ 16½ 18½ 20½ 22½ 24½ 26½ 28½ 30½ 32½ 34½
j₂ 1½ 3½ 5½ 7½ 9½ 11½ 13½ 15½ 17½ 19½ 21½ 23½ 25½ 27½ 29½ 31½ 33½

FIGURE 1

states.[2] Here it is not possible to distinguish which of the *P* branches is P_1 and which P_2 in the same way this is done for the (11,11) band, as explained below. In these representations, a single line may occupy more than one position, according to the value of *j* assigned to it, and in

cases where the combination principle could not be applied, the position was chosen that it lies on a smooth curve. However, in the region $j_1 = 17^1/_2$ to $22^1/_2$ of curve c no regularities could be detected, and hence in this part each line has been represented with all the j values for which it would lie on the figure. The formula used in drawing curve c was

$$\nu = 25{,}289.61 - 3.2570j_1 - 0.04834j_1^2 - 3.04 \times 10^{-5} j_1^3 - 0.890 \times 10^{-6} j_1^4.$$

It will be evident that in the absence of disturbing factors in the unperturbed state these curves also represent deviations of the *terms* from a regular formula. Since there are known to be no irregularities in b^2S, $n = 11$, curve a may be taken as representing term deviations, if the sign of $\Delta\nu$ is changed.

TABLE I

$\omega_0[1-2x(n+1/2)]$	a^2S VIBRATIONAL TERM	n	$\omega_0[1-2x(n+1/2)]$	$^2P_{3/2}$	^2P VIBRATIONAL TERMS $^2P_{1/2}$	n
2041	2,041	1				
2014	4,056	2				
1992	6,049	3				
1965	8,014	4				
1938	9,953	5				
1912	11,865	6				
1885	13,751	7		14,374	14,430	0
1858	15,609	8	1715	16,089	16,145	1
1831	17,440	9	1688	17,777	17,833	2
1804	19,245	10	1661	19,438	19,494	3
1777	21,023	11	1634	21,072	21,128	4
1750	22,773	12	1607	22,679	22,735	5
1723	24,497	13	1580	24,259	24,315	6
1696	26,194	14	1553	25,812	25,868	7
1670	27,864	15	1526	27,338	27,394	8

Curves of the same characteristic form as these apparently apply to a number of perturbations in other band systems. Thus, for example, in the N_2^+ bands, which also result from an electron transition $^2S \longrightarrow {}^2S$, a perturbation similar to the above has been found,[3] although the shape of the curve of deviations was not discussed. Probably the first evidence that perturbations may have this form was obtained by Birge,[4] in a study of the (2,2) band of the violet CN system. A number of irregularities were detected, which undoubtedly are due to displacements of the above type in the initial levels, $n = 2$, of b^2S.

An unusual feature of the perturbations in the state a^2S (curve a) is that they occur in the normal state of the molecule, whereas all perturbations hitherto known are connected with deviations of the terms of an excited state. It seemed, therefore, of interest to examine the situation in detail, to ascertain if possible the cause of this violation of the general rule. It then appeared that the 11th vibrational term is of greater energy

(referred to the $n = 0$ level of a^2S) than the lower terms in another known excited state, ^2P. On plotting the energy levels, it was seen that the vibrational level $n = 11$ in a^2S very nearly coincides with the level $n = 4$ of the ^2P state. Unfortunately the absolute values of the high-n terms of a^2S could not be calculated with any great accuracy from the existing data, but a fair approximation was obtained by assuming Kratzer's formula,[5] $\omega_n = 2055.64 - 27.50n$ to $n = 2$ and the formula obtained from the "tail" bands,[2] $\omega_n = 2059.98 - 26.89n$ thereafter. The levels of the ^2P state were obtained from the data of Heurlinger[6] on the band heads of the red CN system which arise in the transition $^2P \longrightarrow a^2S$. The calculated energy values (in cm.$^{-1}$) are collected in table 1.

The proximity of the 4th vibrational term in the ^2P state to the perturbed term in a^2S led us to an investigation of the structure of one of the

TABLE 2

j_2	(A) Δ_2F_2'' (VIOLET CN)	(B) $R_1(j) - Q_{12}(j+1)$ (RED CN)
$1^1/_2$	18.82	18.75
$2^1/_2$	26.09	25.89
$3^1/_2$	33.42	33.36
$4^1/_2$	40.84	40.65
$5^1/_2$	48.26	48.12
$6^1/_2$	55.64	55.63
$7^1/_2$	62.98	63.01
$8^1/_2$	70.42	70.22
$9^1/_2$	77.80	77.85
$10^1/_2$	85.16	85.44
$11^1/_2$	92.57	92.85
$12^1/_2$	99.92	99.97
$13^1/_2$	107.41	107.57
$14^1/_2$	114.81	114.92
$15^1/_2$	122.06	121.92
$16^1/_2$	129.71	129.59

bands of the red system having $n' = 4$, to see if a corresponding perturbation occurs in the rotational terms in ^2P having $n = 4$. The red system is being investigated by Roots and Mulliken, who kindly furnished a spectrogram of the (4,2) band. The band structure is of the somewhat complex type characteristic of a $^2P \longrightarrow {}^2S$ transition,[7] but it was soon apparent, from the failure of the usual methods of identifying the series in a band, that a perturbation is present in the $^2P_{3/2} \longrightarrow {}^2S$ (low-frequency) sub-band. By means of the combination principle, using the term-differences in a^2S, $n = 2$, known from Heurlinger's measurements of the violet bands,[8] it was first found that the branches, Q_{12} and R_1, are entirely regular. The agreement of the combination differences $R_1(j) - Q_{12}(j+1) = \Delta_2F_2''(j)$ with those obtained from Heurlinger's data are given in table 2, columns (A) and (B).

On the contrary, the Q_1 branch (and probably also the P_{12} branch, the lines of which were too faint for measurement) shows a perturbation, which was detected in the following way. If the σ-type doubling into F_A and F_B states be neglected, we could ordinarily predict the frequencies of the Q_1 lines by the relation $Q_{12}(j) + \Delta_1F_1''(j) = Q_1(j)$. Upon calculation of these frequencies, it was found that no line was close to the predicted position for j between about $12^1/_2$ and $16^1/_2$. However, there were lines in this region which were not included in other branches of the band. The differences between the frequencies of these lines and the calculated frequencies of the Q_1 lines were then plotted against j, and the dotted curve of figure 1 *b* was obtained. In figure 1, the sign of $\Delta\nu$ is changed to make

TABLE 3

	(A)	(B)	(C)	(D)		(E)	
j_1, j_2	Q_{12}(OBS.)	Δ_1F_1''(CALC.)	Q_1(CALC.)	Q_1(OBS.)		$\Delta\nu$(OBS.$-$CALC.)	
$1^1/_2$	17,001.03	7.42	17,008.45	17,008.61		+0.16	
$2^1/_2$	16,997.61	11.13	17,008.74	17,008.96		+0.22	
$3^1/_2$	16,993.61	14.84	17,008.45	17,008.61		+0.16	
$4^1/_2$	16,989.05	18.55	17,007.60	17,007.67		+0.07	
$5^1/_2$	16,983.90	22.26	17,006.16	17,006.05		−0.11	
$6^1/_2$	16,977.84	25.97	17,003.81	17,003.88		+0.07	
$7^1/_2$	16,971.26	29.67	17,000.93	17,001.03		+0.10	
$8^1/_2$	16,964.17	33.38	16,997.55	16,997.61		+0.06	
$9^1/_2$	16,956.24	37.08	16,993.32	16,993.61		+0.29	
$10^1/_2$	16,948.11	40.78	16,988.89	16,989.05		+0.16	
$11^1/_2$	16,939.11	44.48	16,983.59	16,983.90		+0.31	
$12^1/_2$	16,929.56	48.18	16,977.74	16,978.65	973.45	+0.91	−4.29
$13^1/_2$	16,919.53	51.88	16,971.41	16,974.60	969.60	+3.19	−1.81
$14^1/_2$	16,908.79	55.58	16,964.37		963.52		−0.85
$15^1/_2$	16,897.45	59.27	16,956.72		956.24		−0.48
$16^1/_2$	16,885.75	62.96	16,948.71		948.11		−0.60
$17^1/_2$	16,873.23	66.64	16,939.87		939.46		−0.41
$18^1/_2$	16,860.25	70.33	16,930.58		930.16		−0.42
$19^1/_2$	16,846.75	74.01	16,920.76		920.35		−0.41

the term deviations comparable with those of curve *a*. The numerical values are given in table 3, columns (A), (B), (C) and (D). When these lines are assigned to the Q_1 branch every measured line of the band is accounted for. In the above computation, values of $\Delta_1F_1''(j)$ were obtained from the equation $\Delta_1F_1''(j_1) = 2B''(j_1 + {}^1/_2) + 4D''(j_1 + {}^1/_2)$,[3] with $D'' = -6.453 \times 10^{-6}$ and $B'' = 1.8554$, as evaluated by least squares, using the values of Δ_2F_1'' from Heurlinger's data and excluding those which are obviously not reliable.

During the present investigation, an important article by Kronig[9] appeared, in which the origin of perturbations is discussed from the standpoint of the wave mechanics. The principal results of this treatment are the following: (1) Perturbations occur when two terms of equal j in two different electronic states have nearly the same energy. It will be ob-

served that the two perturbations shown in figure 1 *a* and *b*, although not entirely symmetrical, occur at about the same value of j. (2) The quantum number corresponding to orbital angular momentum along the internuclear axis, σ_k, must not differ by more than 0, ± 1 for the two states. ^2S and ^2P states fulfil this condition. (3) The electronic states involved must have the same multiplicity. (4) Both terms must be either "odd" or "even." In this requirement we find the explanation of the fact that only the Q_1 (and presumably the P_{12}) branch is perturbed, while the other two branches are regular. The double character (F_A, F_B) of the rotational terms in ^2P states is well known, and it has recently been shown[10] that for a given rotational level, the two components represent opposite symmetry characteristics, i.e., one is "even," the other "odd." Therefore the Q_{12} and R_1 branches, which have F_B initial states, are not perturbed, even through Q_1, which comes from an F_A level, is markedly affected by near coincidence with a ^2S term. The ^2S terms are also double, but here the two components of a given level are either both "odd" or both "even." This kind of doubling arises from the parallel (F_1) and antiparallel (F_2) orientation of the electron spin with respect to the nuclear angular momentum, and the theory further predicts that only F_2 terms in the ^2S state will be perturbed by a $^2P_{1/2}$ term, and only F_1 terms by a $^2P^3/_2$ term, when the ^2P state is inverted as it probably is here. Therefore the ^2S terms which are *not* perturbed at $j = 12^1/_2$ (Fig. 1, curve *a*) should be F_2, and the designations of the lines by their appropriate subscripts are as given in the figure.

It thus appears that Kronig's theory is supported by our verification of several important predictions. Although his formulae cannot be applied to a quantitative calculation of the perturbation curve in this case, they yield curves of the characteristic type shown in figure 1, as Kronig has shown (loc. cit., Fig. 1). It is notable, however, that in figure 1 a given value of j_1 is in several cases represented by *two* terms. The cause of this splitting is obscure,[15] since presumably the only types of degeneracy inherent in these terms would on removal yield a large number of components. The writers believe that all perturbations now known can be represented by such curves, and on this basis have undertaken a study of perturbations in several other band systems (SiN, CO, N_2^+, BeO, HgH^{--}). In the Ångström bands of CO, we have found several large perturbations of the above type, which were not recorded by Hulthén[11] in his analysis. Plates have been made available through the kindness of Kemble, Mulliken and Crawford, which show the Zeeman effect of these bands under high dispersion, and it is planned to make a thorough study of the effect of a magnetic field on the perturbations. Several irregular Zeeman effects of lines of high j have already been noted by Crawford.[12] These results will be given in a succeeding paper.

In conclusion, it might be mentioned that we have examined a case where perturbations might be expected to occur by Kronig's theory, but do not. In NO, the ^2S state lies very close to the upper ^2P state, and a coincidence of terms having the same j might be anticipated. However, an accurate calculation, using the data of Guillery,[13] and of Jenkins, Barton and Mulliken[14] shows that this does not occur, at least for any terms which are involved in the emission of the β and γ systems.

We are indebted to Professor R. S. Mulliken for suggestions in connection with this investigation.

[1] *Bull. Nat. Res. Council*, **57**, p. 90 (1927).
[2] F. A. Jenkins, *Phys. Rev.*, **31**, 539 (1928).
[3] M. Fassbender, *Zeits. Physik*, **30**, p. 83, fig. 2 (1924).
[4] R. T. Birge, Ref. 1, p. 90, fig. 6.
[5] A. Kratzer, *Ann. Physik*, **71**, 72 (1923).
[6] T. Heurlinger, *Zeits. Physik*, **1**, 82 (1920).
[7] F. A. Jenkins, these PROCEEDINGS, **13**, 496 (1927). The notation given in this reference will be used in the following discussion.
[8] Heurlinger, *Dissertation*, Lund (1918).
[9] R. de L. Kronig, *Zeits. Physik*, **50**, 347 (1928).
[10] Kronig, *Ibid.*, **46**, 814 (1928).
[11] Hulthén, *Ann. Physik*, **71**, 41 (1923).
[12] F. H. Crawford, *Phys. Rev.*, **33**, 353 (1929).
[13] M. Guillery, *Zeits. Physik*, **42**, 121 (1927).
[14] F. A. Jenkins, H. A. Barton and R. S. Mulliken, *Phys. Rev.*, **30**, 150 (1927).
[15] According to a somewhat different interpretation of perturbations suggested to the writers by Prof. E. C. Kemble, the two components are not only accounted for, but definitely required. This will be discussed in our next article on this subject.